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Non-Oxidative Methane/Methanol mixture reforming over Mesoporous Ni-Cu/Al_2O_3 co-doped Catalyst for cleaner hydrogen production

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EXTENDED ABSTRACT

Hydrogen is often considered as a promising alternative energy carrier and clean fuel. Hence, many efforts are directed in developing efficient, economic and green approaches for hydrogen production. Thermo catalytic decomposition over Ni supported catalyst has gained abundant interest in producing hydrogen and elemental carbon by non-oxidative decomposition of various hydrocarbons and their mixtures [1]. The aim of this presented research work it to develop highly efficient and stable promoted catalyst and to explore their activity towards methane/methanol mixture decomposition. This research is based on the profound analysis of published work, which allows selection of appropriate methods and material for this research. 50%Ni/Al_2O_3 and 50%Ni-15%Cu/Al_2O_3 were synthesized by wet impregnation method and after that the interfacial properties of the catalyst were studied by employing various analytical techniques [2]. The stoichiometric amounts of Ni $(NO_3)_2.6H_2O$, Cu $(NO_3)_2.3H_2O$ and γ-Al_2O_3 were used in this research study. Furthermore, N_2 as an inert gas, H_2 as activation gas and 2%CH_3OH/CH_4 was employed as feedstock for thermo catalytic decomposition reaction.

The characterization of the calcined catalyst was completed by using BET, TGA, TPR, XRD and FESEM while the post reaction analysis of the spent catalyst was done by FESEM, Raman spectroscopy and TEM. It was reported that the successive addition of metals on γ-Al_2O_3 support caused a decline in the surface area of Cu promoted catalyst due to agglomeration of particles and partial coverage of support pores by metal precursors. The surface area changed from 5.15 to 4.52 m^2g^{-1} and pore volume from 8.8 to 21.3 nm by impregnating 15% Cu on 50% Ni/Al_2O_3 [3]. TGA analysis reveals that three-stage weight loss was observed including the evaporation of metal hydrates from nano material and conversion of metal nitrates into respective oxides. It was forecasted that the degree of reducibility was improved by the addition of Cu on the Ni-based catalyst by TPR results as the H_2 peaks were shifted towards lower temperature. XRD analysis reveals that the relative peaks of NiO and CuO overlapped each other at 2θ= 37.4°, 44°, 64.3°, 75.3° and 79° that explained the formation of mixed oxides and successful impregnation of Cu on Ni/Al_2O_3. Both synthesized catalysts possessed nano structure having a particle size ranging from 50−200 nm. The catalytic activity of the synthesized materials was evaluated by using high temperature fixed bed catalytic reactor (Model No: GT1000) (L=17 in and O. D= 3/8 in). The performance analysis of both synthesized catalysts was explored at the same set of reaction parameters (W_C 0.1 g, GHSV 18,000 mL g_{cat}^{-1} h^{-1}, R_T 1023 K) and was evaluated solely based on methane conversions. The composition of post reaction gaseous products was analyzed by Agilent 7820A series gas chromatography equipped with both thermal conductivity (TCD) and flame ionization (FID) detector. He used as a carrier gas with an effective

column temperature of 393 K and flow rate of 20 mL min^{-1}. The ni-based catalyst is subjected to an early deactivation after TOS 4 h due to encapsulation of carbon on the surface of the catalyst [4]. Surprisingly, the stability of the catalyst was improved to 6 h after impregnating 15%Cu on Ni/Al_2O_3 while on the other end the methane conversions also enhanced from 25% to 75%. It has been reported that though Cu is inactive in methane reforming reactions, but its high affiliation with carbon restricts its growth on the active sites of the catalyst resulting in the prolonged stability and activity of the bimetallic catalyst [5]. Moreover, reaction temperature and gas hour space velocity effected methane conversions over $50\%Ni\text{-}15\%Cu/Al_2O_3$. The surface morphology of the fresh $50\%Ni\text{-}15\%Cu/Al_2O_3$ and XRD analysis has been shown in Figs 1 (a) and (b) respectively. The mechanism of methanol decomposition is very interesting. Apart from the decomposition of methanol into syngas a major product, a series of other reactions including water gas shift reaction, reverse water gas shift reaction, water gas reaction, boudouard reaction and methanation reaction also occur. So, by visualizing the stated reactions occurring, a series of the hypothesis can be assumed. One of the most critical supportive discussion relating to the simultaneous regeneration of the catalyst can be made. The catalyst can be regenerated by H_2O regeneration, CO_2 regeneration and O_2 regeneration in which the carbon is treated with H_2O, CO_2 and O_2 [6]. So, in the current study, the steam produced during water gas shift reaction oxidized the carbon deposited as carbon nano fibers into synthesis gas. CO_2 also plays a vital role in catalyst regeneration by converting the elemental carbon into CO. It should be worth noted that the simultaneous catalytic decomposition of mixture and regeneration of the catalyst increase the catalyst stability and allows Ni to remain active and fresh for methane dissociation.

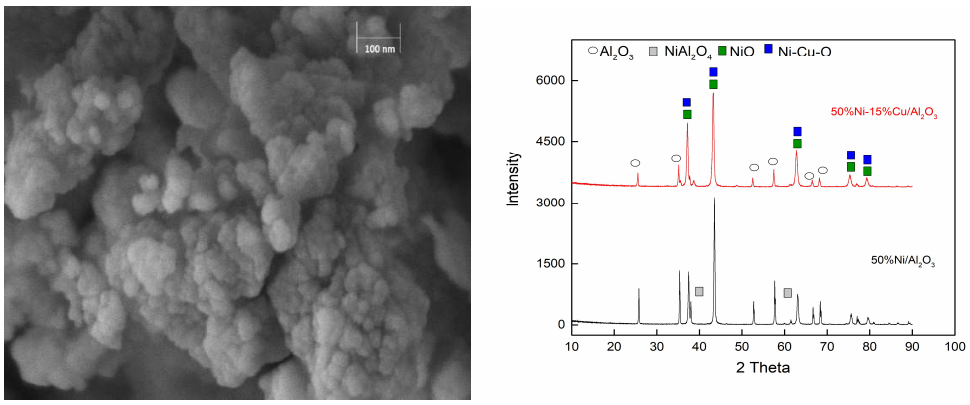
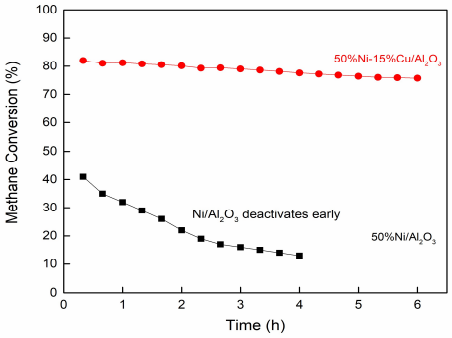


Figure 1: Analysis of $50\%Ni\text{-}15\%Cu/Al_2O_3$ (a) FESEM Image of Fresh (b) XRD analysis of calcined catalyst

It should be noted that apart from H_2 as a gaseous product, elemental carbon has also been produced as by-product. Carbon nano fibers with a diameter of few nano meters can be easily scrutinized deposited on the surface of the catalyst. The carbon nano fibers were formed in interwoven hierarchy making it nearly impossible to estimate the precise length and diameter of them. Moreover, these carbon fibers are seen to be long and entangled in shape with diverse diameters. The morphology of the deposited carbon is strongly dependent on the reaction parameters including reaction temperature, gas hour space velocity and metal loadings. Furthermore, it was observed in the FESEM results that wider CNF were deposited on $50\%Ni{-}15\%Cu/Al_2O_3$ as compared to $50\%Ni/Al_2O_3$. The performance evaluation of both synthesized catalysts over set of conditions as W_C 0.1 g, GHSV 18,000 mL g_{cat}^{-1} h^{-1} and R_T 1023 K has also been explained in Fig 2 (a) while the morphology of spent carbon deposited on the surface of $50\%Ni{-}15\%Cu/ Al_2O_3$ has been shown in Fig 2 (b).



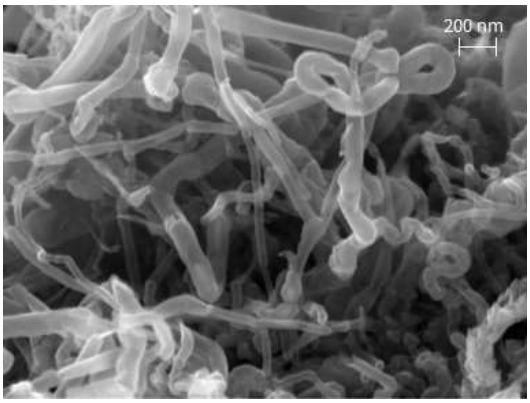


Fig 2: Analysis of 50%Ni-15%Cu/Al_2O_3 (a) Performance Analysis (b) FESEM Image of Spent Catalyst

Keywords: Thermo catalytic decomposition; alloy; Ni; Cu and carbon nano fibers.

References

[1] W. Ahmed, A. E. Awadallah, and A. A. Aboul-Enein, "Ni/CeO_2–Al_2O_3 catalysts for methane thermo-catalytic decomposition to CO x-free H_2 production," *International Journal of Hydrogen Energy,* vol. 41, pp. 18484-18493, 2016.

[2] A. Al-Fatesh, A. Fakeeha, W. Khan, A. Ibrahim, S. He, and K. Seshan, "Production of hydrogen by catalytic methane decomposition over alumina supported mono-, bi-and tri-metallic catalysts," *International Journal of Hydrogen Energy,* vol. 41, pp. 22932-22940, 2016.

[3] A. Rastegarpanah, F. Meshkani, and M. Rezaei, "Thermocatalytic decomposition of methane over mesoporous nanocrystalline promoted Ni/MgO· Al_2O_3 catalysts," *International Journal of Hydrogen Energy,* 2017.

[4] N. Bayat, M. Rezaei, and F. Meshkani, "Methane decomposition over Ni–Fe/Al_2O_3 catalysts for production of CO x-free hydrogen and carbon nanofiber," *International Journal of Hydrogen Energy,* vol. 41, pp. 1574-1584, 2016.

[5] N. Bayat, M. Rezaei, and F. Meshkani, "Methane dissociation to COx-free hydrogen and carbon nanofiber over Ni-Cu/Al 2 O 3 catalysts," *Fuel,* vol. 195, pp. 88-96, 2017.

[6] H. F. Abbas and W. W. Daud, "Hydrogen production by methane decomposition: a review," *International Journal of Hydrogen Energy,* vol. 35, pp. 1160-1190, 2010.